

The 9<sup>th</sup> Asia-Oceania Symposium on Fire Science and Technology

## Thermal decomposition extent of duff due to surface forest fire

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In ground fires, duff is thermally decomposed and smoldering combustion occurs. Duff is also partially decomposed by surface fire heating and the decomposition percentage is a clue to surface fire severity assessment. This article investigates thermal oxidative decomposition characteristics of Northeast Chinese forest duff samples, with and without surface fire heating effect, by thermogravimetry. The curves of all duff samples showed four stages, *i.e.* moisture evaporation, duff devolatilization, char oxidation and nearly-invisible inorganic minerals decomposition. The effect of surface fire heating was estimated by comparing the mass loss ratio of the devolatilization stage to the char oxidation stage and it was found that nearly 27.4% of original duff was decomposed by surface fire heating.

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Selection and peer-review under responsibility of the Asian-Oceania Association of Fire Science and Technology

**Keywords:** Duff; Thermal decomposition extent; Surface fire severity

**1. Introduction**

Daxing'anling forests in Northeast China are covered by fire-prone tree species, such as Mongolian scotch pine (*Pinus sylvestris* Linn. var. *mongolica* Litv.) and Dahurian Larch (*Larix gmelinii* Rupr). Forest fires in Daxing'anling forests, by natural or anthropogenic causes, are mostly flaming surface forest fires, which sweep shrubs and fallen litters quickly. During surface fire, duff underneath litters are heated and partially burned. Organic matters in soil may be lost, too. The extent of duff burned during surface fire depends on the heating intensity and surviving time of surface fire. After surface fire passing, the extent of duff burned provides some clues to surface fire severity. In some studies, duff is also considered to be of soil organic matters (SOM). Since SOM plays an important role in soil exchange, the effect of fire on SOM is studied intensively [1], of which determination of SOM losses by forest fires is of paramount importance to know soil degradation [2].

During surface fire, duff or organic matters in soil underneath the litter are heated. After moisture removal, thermal decomposition follows. For a similar forest material to duff, forest peat, it is reported that thermal oxidative decomposition of Chinese forest peat presents two main reaction stages: the stage of organic matter decomposition (427–575 K) and char oxidative combustion (575–800 K) [3]. Peat samples from Scotland and Siberia also present similar decomposition behavior, with the separation temperature of the two stages to be about 640 K [4]. If duff decomposes like peat, which will be verified later in this paper, duff will also undergoes two-stage decomposition process under surface fire heating. If duff temperature during the heating is lower than the separation temperature of the two stages, char oxidative combustion will not occur and charcoal will be found in duff after surface fire passing. For reference, there are many studies on the temperature profiles of soil under field surface fire heating or simulated fire heating. It is reported that soil surface temperature reaches 170–235 °C or 322–543 °C for different fire severities [5]. However, the temperature decreases quickly from soil surface to in-depth soil.

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Heat transfer models predict the peak temperature at 1-cm depth of soil is commonly lower than 350 °C and the lethal heat penetration depth (the depth at which a temperature of 60 °C is achieved) is commonly lower than 5cm in simulated surface fire heating [6]. If the moisture content increases, the soil temperature will decrease rapidly. During the surface fire, duff is wet and covered by debris and ash and therefore its temperature is not high enough. In most cases, it undergoes slow thermal decomposition at relative low temperature. The char oxidative combustion process seldom happens under this circumstance.

It is hard to determine the decomposition extent of duff under surface fire heating. For SOM, its loss due to wildfire is often calculated by calorimetric methods. Often the DSC (differential scanning calorimetry) curves of unburnt and burnt soil samples are compared to calculate the combustion enthalpy loss, or TG (thermogravimetry) curves of unburnt and burnt soil samples are compared to calculate the difference of weight loss [2, 7, 8]. Because duff only undergoes the first-stage decomposition and charcoal remains, the methods for SOM may underestimate the decomposition extent of duff. For example, assuming duff totally finishes the first stage decomposition, the decomposition extent of duff will be 100%. However, if it is estimated by the methods for SOM, the extent will be 100% minus the percentage of charcoal mass to original duff mass, lower than 100%.

This paper will study thermal oxidative decomposition of Northeast Chinese forest duff by the non-isothermal TG method. The effect of surface fire heating on duff decomposition characteristics will be also discussed. Based on the difference of TG curves, a simple method is proposed to determine the extent of duff decomposition caused by surface fire heating.

## 2. Materials and methods

### 2.1. Sample collection

The forest duff samples were collected from three sites of the boreal forests of north-east China, which are at (E123°44'57.5", N51°57'55.8"), (E122°12'27.9", N51°51'20.3") and (E124°05'18.8", N50°17'53.1") respectively. The first two sites were located in virgin forests and the third in plantation forests. All these sites presented mild-slope landform and had similar vegetation. Mongolian scotch pine (*Pinus sylvestris* Linn. var. *mongolica* Litv.) was the dominant arbor and some shrub species (such as *Ledum palustre* Linn.) and grass species (such as *Deyeuxia langsdorffii* (Link) Kunth) were found above the ground. The forest duff was mainly originated from the needles and bark of pines, the leaves of shrubs and the dried grass, together with some other vegetation materials.

Table 1. The details of the sampling process

Sampling sites				Sampling time	Sample identification	Sample Symbol
No.	Description	longitude	latitude			
Site 1	Virgin pine forest in Huzhong, China.	E123°44'57.5"	N51°57'55.8"	July 13, 2008	0-5 cm duff	HD1
	Surface wildland fire occurred in April, 2008.				5-12 cm duff	HD2
	The duff depth is about 12 cm					
Site 2	Virgin pine forest in Huzhong, China.	E122°12'27.9"	N51°51'20.3"	July 14, 2008	0-20 cm duff	HD3
	Surface wildland fire occurred in June, 2000.					
	The duff depth is about 20 cm.					
Site 3	Plantation pine forest in Jiagedaqi (more than 20 years) , China.	E124°05'18.8"	N50°17'53.1"	July 12, 2008	0-3 cm duff	JD1
	Not burned by wildfire.				3-5 cm duff	JD2
	The duff depth is about 5 cm.				Organic soil	JS
	Soil is also sampled for comparison.					

The sampling work was finished in July, 2008. The first site was swept by surface forest fire in April of that year, and the second by surface fire in June, 2000. In the first site, a few fresh green grasses were growing and shrubs were still not regenerated, while in the second site, the shrubs, grasses and young trees were seen everywhere because of eight years natural resilience. In both sites, the floor duff was seen to be burned partially by fire and turned black, in which some small charcoal particles were found. The charcoal particles in duff surface might be residues from the burned shrubs and trees.

However, the duff below the surface also contained very small charcoal particles, which could be originated from the decomposition or burning process of duff itself. The third site was not affected by fire and duff was mainly from pine needles, after many years of natural fermentation.

Before formal sampling, the litter and debris above the duff (about 1cm) were removed, and then the depth and layer structure of forest duff of each site were estimated. According to the depth and layer structure, forest duff was sampled layer upon layer in formal sampling process. In each site, four plots of 20 cm×20 cm were selected to collect duff. The samples were collected at the same layer from four lots and after mixing, sealed in the plastic bags for transportation. The duff in the first site showed a depth of 12 cm and two-layer structure by different duff color and texture. The duff in the second site was 20 cm deep with nearly same appearance. And the duff in the third site was two layered with different fermentation degree. In this site, the organic soil below the duff was also sampled for comparison. Table 1 summarized the details of the sampling process and defined the shortening symbols for the samples. HD1 is lightly to moderately decomposed upper duff (the fermentation layer) and looks black with small pieces of roots. HD2 is more highly decomposed lower duff (the humus layer) and looks grey. HD3 is a mixture of brown duff blocks with small particles of bark pieces. JD1 contains many long pine needles; however, there are only small pieces of pine needles in JD2. JS is soil sample which looks dark red.

## 2.2. Sample preparation

In the laboratory, about 1kg sample was taken from each sealed bag and placed in the plates. After removing the obvious tree roots and stones, the samples were dried 24 h at 353 K in the oven. Then they were grounded to small particles and sieved. The particles with sizes between 100 and 150  $\mu\text{m}$  were subjected to thermal analysis.

## 2.3. TG/DTG measurements

TG and derivative thermogravimetry (DTG) were used to characterize thermal oxidative decomposition of the samples. The thermal runs were performed on a Shimadzu DTG-60H analyzer (weight readability: 1  $\mu\text{g}$ ). About 10mg of samples for each analysis were evenly distributed over the open alumina crucible and heated at a heating rate of 10 K/min from room temperature to 1073K, in air atmosphere at a flow rate of 50 ml/min (at normal temperature and atmospheric pressure). The heating rate is comparable to that in smoldering fire and is used in peat decomposition studies [4]. Two runs were performed with the same experimental conditions on TG analyzer and the experiment reproducibility was verified.

## 3. Results and discussion

### 3.1. Characteristics of TG-DTG curves

Figure 1 presents the TG and DTG curves of duff samples and soil sample in air atmosphere at 10 K/min. The TG curves (Fig. 1-A) shows that after thermal decomposition, soil sample losses the least mass and the residue mass percentage is as high as 81.3%. Duff JD2 has residue mass of 23.2% and JD1 of 17.4%. The results indicate that the inorganic content of duff and soil below forest ground surface increases with the increment of depth. The similar tendency is found for HD1 and HD2, as HD1 has the lowest residue mass of 17.0% and HD2 has the second highest residue mass of 42.6%. The residue mass of HD3 is 26.3%, which is nearly the average percentage of residue masses of HD1 and HD2. The duff samples after surface fire heating generally has a little more residue mass percentage than the virgin duff samples.

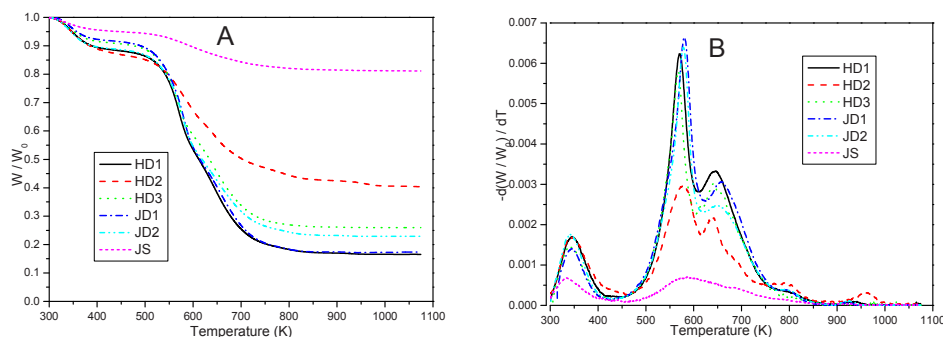


Fig. 1. TG (A) and DTG (B) curves of thermal oxidative decomposition of duff and soil (normalized by the initial sample weight  $W_0$ ).

In the DTG (Fig. 1-B) curves, duff samples present similar mass loss processes while soil sample shows somewhat different processes in the temperature range of about 450-850 K. During 450-850 K, the mass loss rate curves of duff samples present two consecutive mass loss peaks while the curve of soil sample only present one mild peak.

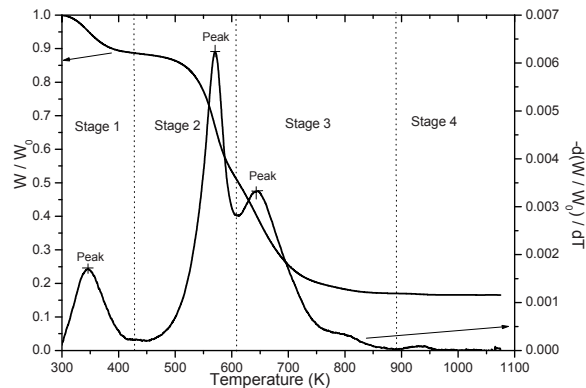


Fig. 2. Stage division of TG-DTG curves of duff samples (HD1 as an example).

In order to characterize the mass loss rate curves of duff samples, Fig. 2 shows the stage division for duff samples and Table 2 gives the detailed parameters. In this figure, the mass loss process of duff is divided into four stages. The first stage occurs in temperatures of 300-450 K, with the temperature of peak mass loss rate to be about 340 K. This mass loss stage is often attribute to moisture evaporation [3, 9]. In Stage 2, the mass loss rate increases sharply to the highest peak value at about 570 K. The peak value of mass loss rate for HD1 is  $0.00623 \text{ K}^{-1}$  and the mass loss reaches 37.6% in this stage. Above 608 K, Stage 3 follows Stage 2 and contributes to 34.1% mass loss for HD1. Over 894 K, the mass loss process is almost finished in Stage 4, leaving inorganic residues. Some inorganic minerals decompose in such high temperature and some very small mass loss process is seen in this stage, especially for HD2.

Table 2. Characteristic parameters of the TG-DTG curves of thermal decomposition of duff and soil samples in air

Sample	Stage 1			Temperature Stage 2 at separation			Temperature Stage 3 at separation			Temperature Stage 4 at separation			
	Maximum mass loss rate (MMLR) /K	Peak loss temperature at MMLR /K	Mass loss (P <sub>1</sub> ) %		Maximum mass loss rate (MMLR) /K	Peak loss temperature at MMLR /K	Mass loss (P <sub>2</sub> ) %		Maximum mass loss rate (MMLR) /K	Peak loss temperature at MMLR /K	Mass loss (P <sub>3</sub> ) %		Remaining mass (P <sub>4</sub> ) %
HD1	0.00170	346.9	11.3	425.9	0.00623	570.1	37.6	608.3	0.00333	645.8	34.1	894.4	17.0
HD2	0.00170	342.4	13.3	455.9	0.00296	577.5	23.1	617.4	0.00217	641.0	21.0	885.8	42.6
HD3	0.00143	344.0	9.0	428.7	0.00581	567.9	33.6	604.9	0.00301	640.5	31.2	887.9	26.2
JD1	0.00139	342.5	8.4	431.4	0.00665	579.7	44.3	624.2	0.00305	658.2	29.9	881.9	17.4
JD2	0.00176	342.2	11.0	428.0	0.00640	578.2	39.8	621.9	0.00248	649.2	26.0	888.9	23.2
JS	0.00067	336.2	5.1	455.4	0.00070	582.3	13.6	-	-	-	-	955.9	81.3

The decomposition behavior of duff is similar to that of peat [3, 4]. The mechanism of each decomposition stage of duff is same with that of peat. Stage 1 refers to moisture evaporation. The organic components in duff or soil are believed to decompose and combust in Stages 2 and 3, which leading to highest mass loss. Stage 2 reflects the mass loss of duff devolatilization and Stage 3 is due to char oxidation.

Soil sample has less organic components than duff samples and thus presents mild mass loss process during 450-850 K. The devolatilization and char oxidation stages are not obvious for soil sample, which may be because the organic components (mainly cellulose, hemicellulose and lignin) in soil have undergone more natural microbial decomposition or

fermentation. Generally lignin is more difficult for natural microbial decomposition than cellulose and hemicellulose and thus the relative contents of lignin will increase after long time natural microbial decomposition [10]. Orfao et al. [11] have pointed out that cellulose and hemicellulose decomposition processes in air exhibit two mass loss peaks while lignin decomposition process shows only one low peak, however, the processes of volatile formation and residue gasification occur simultaneously in the lignin decomposition process. So it can be inferred that soil sample have higher content of lignin and the decomposition process is more likely to present one mild peak like that of lignin.

### 3.2. Effect of surface fire heating on duff thermal decomposition

During spreading surface fire, the litter on the forest floor may burn and heat the underneath duff or soil. The temperature increment of soil during surface fire heating often varies for different soil types, moisture contents and depth. The maximum surface temperatures were reported to be 600 °C for dry soils and 100-200 °C lower for moist soil [12], and the temperatures inside soils decrease very quickly with the increment of depth [6]. In the sampling sites of this investigation, the duff surface was not severely burned. It is reasonably assumed that the duff wasn't heated to very high temperatures and only partial duff was devolatilized by surface fire heating. The devolatilized duff produced small charcoal particles which were observed inside the duff samples. So the duff samples after surface fire heating can be treated as mixtures of original duff and charcoals. According to the results of thermal analysis experiments, the original duff in these samples firstly devolatilize to volatiles and charcoal, and then all the charcoal, generated by original duff decomposition and by fire heating, is oxidized in air atmosphere. The devolatilization process is not affected by charcoal presence. If the original duff in all these collected duff samples exhibits same decomposition behavior, which will be proved in the following, the extent of duff decomposed by surface fire heating can be estimated.

### 3.3. The extent of duff affected by surface fire heating

Since the duff samples have different contents of original duff and Stage 2 in Fig. 2 is due to original duff devolatilization, it is more convenient to normalize the DTG curve by the mass loss of Stage 2 in order to compare the devolatilization behavior of different original duff in all the samples. Fig. 3 presents the results after normalization. This figure presents two-fold information. Firstly, it is clear that the DTG curves in Stage 2 are almost overlapped for all the duff samples, which indicates that the devolatilization behavior of different original duff in these samples is nearly identical. Secondly, the DTG curves in Stage 3 present two categories, one for duff samples with surface fire heating effect and one for samples without fire heating effect. The mass loss and its rate of samples with fire heating effect are higher than those for samples without fire heating effect. The mass loss ratio of Stage 3 to Stage 2 is presented in Fig. 4. For duff samples without fire heating effect, the ratio is averaged to be 0.664. However, for duff samples with fire heating effect, the average value is 0.915. It is obvious that surface fire heating had induced the partial devolatilization of original duff and presence of charcoal in duff samples. Here the percent of the original duff decomposed during surface fire,  $\gamma$  is estimated.

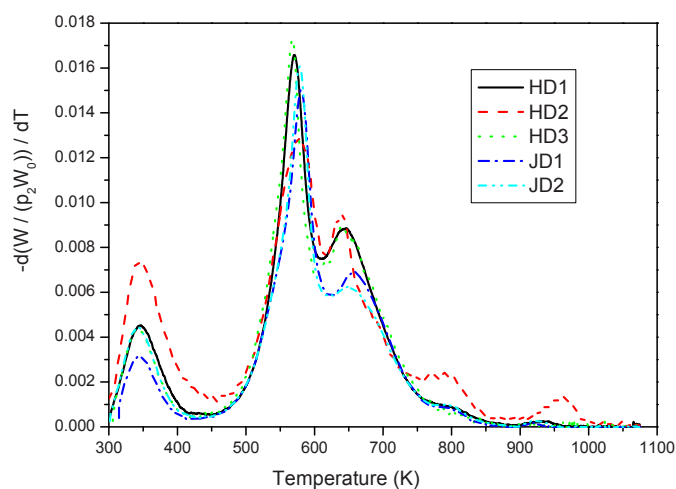


Fig. 3. DTG curves normalized by mass loss in Stage 2 ( $p_2W_0$ ).

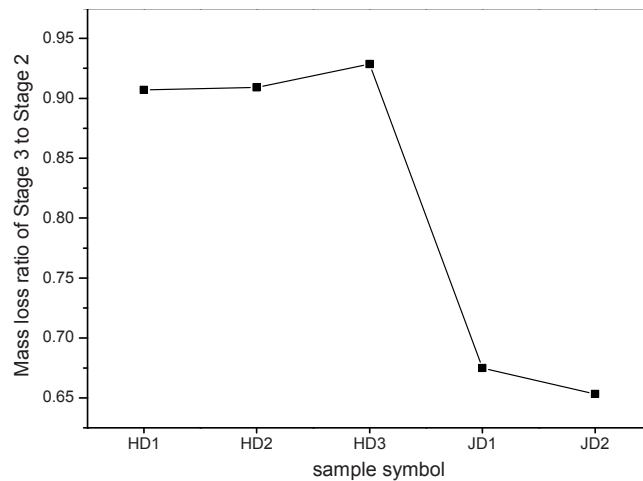


Fig. 4. Mass loss ratio of Stage 3 to Stage 2 in DTG curves.

As stated before, duff thermally decomposes into char and volatiles during the devolatilization process and then char is oxidized in air atmosphere. Denoting that 1 kg duff could decompose to  $x$  kg volatiles and  $y$  kg char, the mass loss ratio satisfies

$$y/x = 0.664 \quad (1)$$

After surface fire, 1 kg of original duff will become a mixture of  $(1-\gamma)$  kg original duff and  $\gamma y$  kg char. During the TG experiments, there will be a mass loss of  $(1-\gamma)x$  kg in Stage 2 and  $(1-\gamma)y + \gamma y = \gamma y$  kg in Stage 3. So the mass loss ratio of Stage 3 to Stage 2 is

$$\frac{y}{(1-\gamma)x} = 0.915 \quad (2)$$

Therefore from Eq. (1) and (2), the value of  $\gamma$  is 27.4%, which means about 27.4% of original duff was decomposed by surface fire heating.

#### 4. Conclusions

In this work, thermal decomposition characteristics of Northeast Chinese forest duff under air atmosphere were investigated by thermal analysis techniques. The DTG curves during devolatilization stage for all duff samples, with and without surface fire heating effect, was found to be almost overlapped after normalization. However, the DTG curves during char oxidation stage showed more mass losses for duff samples with fire heating effect than those without fire heating effect. The result showed that about 27.4% of original duff was decomposed by surface fire heating, which was a clue for surface fire severity assessment.

#### Acknowledgements

This work was sponsored by National Natural Science Foundation of China under Grants 51176179 and 51120165001. H.X.C. was supported by OATF, USTC.

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